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XPS and IR Characterization of Ultra-High Molecular Weight Polyethylene

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Summary

We used x-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to characterize samples of 3-mil thick rolled sheets of ultrahigh molecular weight polyethylene (UHMWPE). The purpose of the XPS work was to determine the surface composition of the UHMWPE and determine if any impurities (particularly halogens) were consistently present of the surface of the sheet. XPS results indicate as-received UHMWPE is reasonably clean, but somewhat inhomogeneous. Some as-received samples contain small amounts of silicon, chlorine, and sodium, while others only contain carbon and oxygen (as expected for ambient exposed plastic). Both ethanol wiping and ethanol sonication effectively remove the Si, Cl, and Na impurities. Additionally, these impurities are not detected by XPS after the top 20nm of material is ablated from as-received sample surfaces. These results suggest the impurities are surface contaminants arising from sample handling and/or ambient exposure. The purpose of the IR work was to collect baseline spectra of the UHMWPE for match factor comparison against known polyethylene materials. The IR spectra for all UHMWPE samples are similar to one another and to known polyethylene materials.

UHMWPE

Rolled sheet samples of 3-mil thick ultra-high molecular weight polyethylene (GUR® 4150, manufactured by Celanese) were obtained from CS Hyde Company. Several sample conditions were characterized in this work. They include UHMWPE samples 1) as-received, 2) ethanol-wiped, 3) ethanol-sonicated (~ 10 minutes at room temperature), 4) aged four months in contact with stainless steel at 70 ^{o}C and 70% relative humidity, and 5) aged four months in contact with beryllium at 70 ^{o}C and 70% relative humidity [aged samples were ethanol wiped prior to aging]. UHMWPE samples were cut from inner portions of the material roll, so that they would presumably have the least exposure to ambient conditions or worker handling.

XPS Results

XPS is a surface-sensitive analytical technique used to determine the elemental composition and chemical valence at the top ~ 5 nm of solid materials. XPS data were collected using a Physical Electronics VersaProbe II system with a base pressure below 1 x 10^{-7} Pa. A monochromated Al kα x-ray source was rastered across 400 x 1200 um area of sample, and photoelectrons were energy sorted using a hemispherical analyzer. Samples were at room temperature. XP spectra are reported in terms of binding energy (BE) and instrument calibration was performed in accordance with ASTM procedure. Elemental analysis was determined from survey scans at high pass energy. Elemental quantification was determined from high-resolution scans at low pass energy. Depth profiling was carried out using 2 kV argon ions. Charge neutralization for insulating samples is accomplished by focusing low energy ions and electrons at the spot of x-ray impingement.

Shown in Figure 1 are XPS survey scans for as-received and ethanol-wiped UHMWPE samples. The 'dirtiest' example of an as-received sample is shown in Figure 1. All prepared samples show the expected high concentrations of carbon (from the polyethylene) and small amounts of oxygen (from ambient exposure). The only impurities detected by XPS on any samples were silicon, chlorine, and sodium. As-received samples were inhomogeneous, with some samples showing only carbon and oxygen and others showing the impurities.
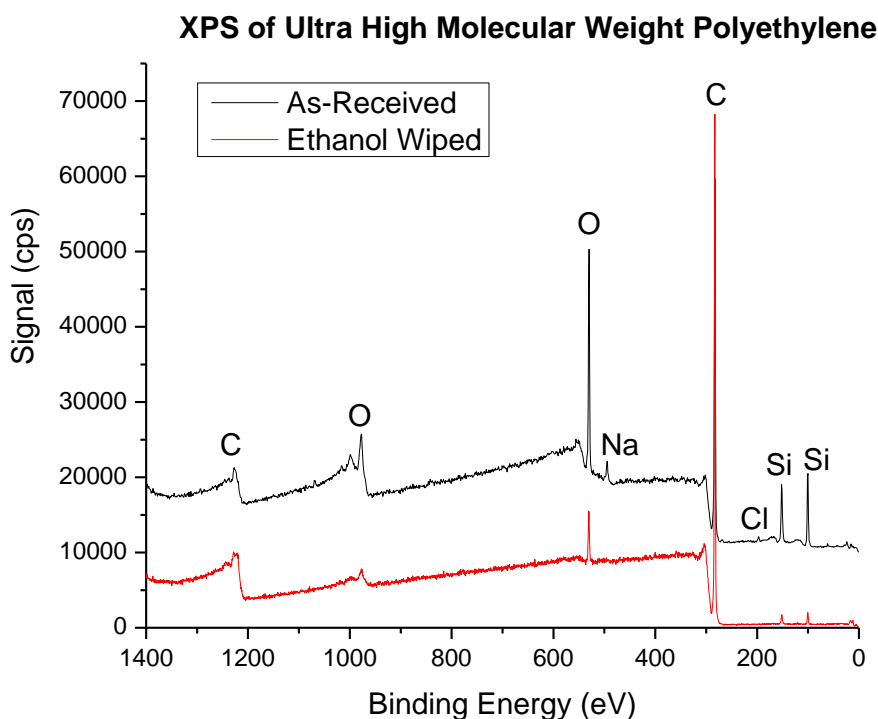

Figure 1: XPS survey scans of as-received and ethanol-wiped UHMWPE.

Elemental compositions of samples as determined by XPS are shown in Table 1. Table 1 includes measurements of the surface composition as well as the sub-surface composition after ion sputtering has removed ~ 20 nm of material. The unsputtered surfaces are reasonably clean; carbon:oxygen

elemental ratios of 90:10 are routinely observed by XPS for uncleaned polymer samples. The presence of Na, Si, and Cl impurities is seen on some areas of as-received UHMWPE and for UHMWPE in contact with beryllium. In these cases, concentrations for both Na and Cl are barely above detectable limits, while O and Si concentrations are considerably higher. Silicon contamination is often associated with sample handling (contact with gloves for example). For all samples very little impurities are observed after removal of the topmost surface. The removal of O, Na, Si and Cl with this light sputtering indicates they are surface impurities.

	C	O	Na	Si	Cl
Surface Composition					
As-received, clean	95	5	0.1	0.2	< 0.1
As-received, dirty	87	10	0.3	3	0.3
Ethanol Wiped	95	4	0.1	1.5	< 0.1
Ethanol Sonicated	98	2	< 0.1	0.1	< 0.1
Aged, SS contact	96	2.5	< 0.1	1.5	< 0.1
Aged, Be contact	85	9	< 0.1	6	< 0.1
Sub-Surface Composition					
As-received, clean	> 99	0.2	< 0.1	0.2	< 0.1
As-received, dirty	99	0.7	0.1	0.2	< 0.1
Ethanol Wiped	> 99	< 1	< 0.1	0	< 0.1
Ethanol Sonicated	> 99	0.5	< 0.1	< 0.1	< 0.1
Aged, SS contact	> 99	0.5	< 0.1	< 0.1	< 0.1
Aged, Be contact	> 99	0.3	< 0.1	0.3	< 0.1

Table 1: Elemental Composition (atomic concentrations) of UHMWPE samples. The sensitivity of elements by XPS is 0.1 atomic % at best.

IR Results

ATR is an infrared vibrational spectroscopy in which light is passed through a crystal to develop an evanescent wave which spills into a sample in contact with the crystal. ATR-FTIR is particularly suited to probing solid materials. ATR-FTIR measurements were collected using a Nicolet Avatar 360 with a Smart DuraSamlIR accessory that uses a single-reflection horizontal diamond ATR. UHMWPE samples were placed directly on the crystal without additional sample preparation. Spectra were collected at 32 scans with 4 cm^{-1} resolution.

Figure 2 shows ATR-FTIR spectra for the UHMWPE samples. The IR spectra show peaks expected for C-H stretching ~ 2900 cm^{-1}, CH2 stretching ~ 1500 cm^{-1}, and CH2 scissoring ~ 700 cm^{-1}. We compared the similarity of IR spectra of samples using match factor (MF) analysis*. In this work we chose ethanol-

wiped UHMWPE as the 'standard' UHMWPE sample because we are using ethanol-wiped UHMWPE in an ongoing contact corrosion study with stainless steel and beryllium substrates. Ethanol-wiped UHMWPE compares closely (MF ~ 96) to polyethylene bags we have previously studied using ATR-FTIR. All UHMWPE samples studied here compare closely to our ethanol-wiped UHMWPE, with MFs ~ 98. Additionally we performed transmission FTIR on mechanically-thinned samples of ethanol-wiped UHMWPE and obtained a match factor of ~ 95 with a polyethylene standard in a commercial FTIR database.
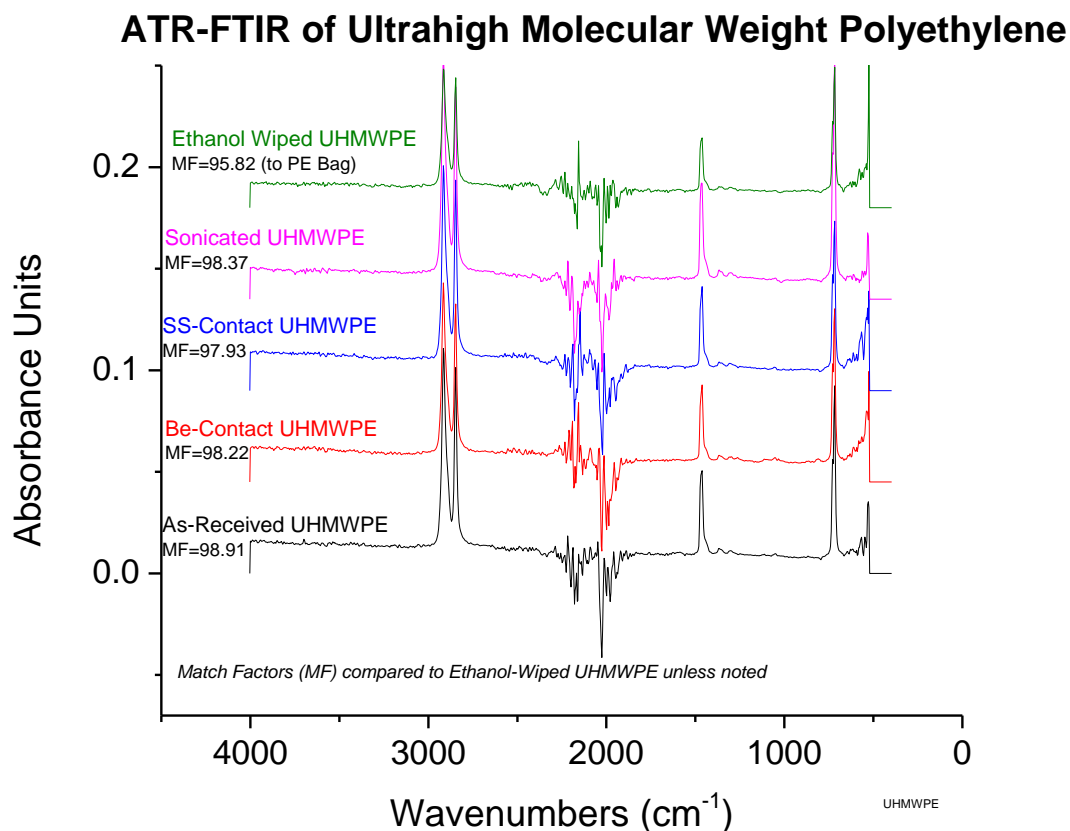

ATR-FTIR of Ultrahigh Molecular Weight Polyethylene

Figure 2: ATR-FTIR of UHMWPE samples.

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*Match factor analysis a mathematical measure of the strength of association between two variables and is a standard tool for the comparison of infrared spectra. Traditionally, the analysis generates a

match factor with a value between 0 and 100 by comparing a given spectrum with a library of known spectra. The higher the match factor, the greater the similarity of the two spectra (and hence two compounds) being compared. Typically, a match factor of greater than 90 is needed to indicate similarity between IR samples. For instance, in analyzing IR data[1], identical compounds nearly always generate match factors above 95, and match factors above 90 indicate homologous compounds. Correspondingly, IR match factors below 90 are indicative of dissimilar compounds.

[1] *Performance Analysis of a Simple Infrared Library Search System*, M. Ruprecht and J. Clerc, *J. Chem. Inf. Comput. Sci.*, 25, pg 241-244, 1985.